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(54) Article comprising conductive polymers and process for making the same.

(57) Polyamides comprising substantial amounts of Nylon-11  
and/or Nylon-12 units are cross-linked by irradiation in the  
presence of an unsaturated cross-linking agent, preferably  
triallyl isocyanurate. The cross-linked products are particu-  
larly useful in the form of heat-recoverable shaped articles,  
eg. heat-shrinkable tubing.

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This invention relates to articles, especially heat-recoverable articles, made from radiation cross-linked polyamides.

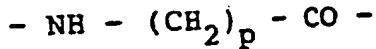
Various attempts have been made to use radiation to cross-link polyamides or to graft-polymerise monomers onto polyamides. Reference may be made, for example to U. S. Patents Nos. 2,858,259, 2,965,553 and 3,681,216 and U. K. Patent No. 1,184,599. However, the known methods suffer from serious disadvantages, for example failure to produce adequate cross-linking, excessive degradation of the polyamide, and impractical processing techniques. As a result, heat-recoverable articles made from cross-linked polyamides have not been available.

We have now discovered that polyundecanoamide and polydodecanoamide (referred to herein as Nylon-11 and Nylon-12 respectively), and copolymers and polymer blends containing substantial proportions of Nylon-11 and Nylon-12, can readily be cross-linked by means of ionizing radiation in the presence of unsaturated radiation cross-linking agents, and that very useful heat-shrinkable articles can be made from the cross-linked products. The cross-linking process can be carried out in air and excellent results can be obtained using small amounts of cross-linking agent and low radiation dosages.

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In one aspect, the present invention provides an article, especially a heat-recoverable article, composed of a radiation cross-linked polymeric composition which

- (a) has been cross-linked by radiation in the presence of an unsaturated radiation cross-linking agent,
- (b) has an  $M_{100}$  value above its melting point of at least 2.1  $\text{kg/cm}^2$ , preferably 2.1 to 10.5  $\text{kg/cm}^2$ , especially 2.6 to 4.2  $\text{kg/cm}^2$ , and
- (c) comprises a cross-linked organic polymer component which comprises at least 80%, preferably substantially 100%, by weight of at least one polyamide consisting essentially of monomer units which are linked to each other through amide linkages, at least 25%, preferably at least 75%, by weight of the monomer units having the formula



where  $p$  is 11 or 12.

In another aspect, the invention provides a process for the manufacture of a cross-linked polyamide article as defined above which comprises the steps of

- (1) melt-shaping a polymeric composition comprising
  - (a) an organic polymer component which comprises at least 80% by weight of at least one polyamide consisting essentially of monomer units which are linked to each other through amide linkages, at least 25%, preferably at least 75%, by weight of the monomer units having the formula  $- \text{NH} - (\text{CH}_2)_p - \text{CO} -$ , where  $p$  is 11 or 12; and

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(b) an unsaturated radiation cross-linking agent for said polymer component; and

(2) irradiating the shaped article prepared in step (1) to effect cross-linking thereof.

A preferred embodiment of the process further comprises the steps of (3) heating the cross-linked article above its melting point; (4) deforming the article while it is at a temperature above its melting point; and (5) cooling the article while it is in the deformed condition; whereby a heat-recoverable article is prepared.

The organic polymer component used in this invention comprises at least 80%, usually at least 90%, preferably at least 95%, especially substantially 100%, of one or more polyamides in which substantially all the monomer units are linked to each other through amide linkages. (Percentages are by weight throughout this specification.) Thus the component may (but preferably does not) contain a small proportion of one or more other compatible polymers, eg. polyethylene. The polyamide contains at least 25%, preferably at least 75%, based on the component, of Nylon-11 and/or Nylon-12 units, i.e. units of the formula - NH -  $(\text{CH}_2)_p$  - CO -, where p is 11 or 12. These units may be present as a homopolymer, or as part of a copolymer, or both. Thus the polymer component may contain 25 to 100%, preferably 75 to 100%, of Nylon-11 or Nylon-12 or both, and 0 to 75%, preferably 0 to 25% of another polyamide, preferably Nylon-6, Nylon-6,6, Nylon-6,9, Nylon 6,10 or Nylon-6,12 or two or more of these.

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Cross-linking agents for use in this invention usually consist of elements selected from carbon, hydrogen, oxygen and nitrogen. The preferred cross-linking agent is triallyl isocyanurate, which we have found to give particularly good results even when used in small amounts and at low radiation doses. Triallyl cyanurate is also very useful, especially when used under conditions which cause isomerisation to the isocyanurate. Mixtures of cross-linking agents can be used. The amount of cross-linking agent used is preferably less than 4%, eg. 0.1 to 4%, particularly less than 2%, eg. 0.1 to 2%, especially about 1%, eg. 0.3 to 1.25%, based on the polymer component.

The polymeric composition may contain other ingredients in addition to the polymer component and the cross-linking agent (or residue thereof after radiation cross-linking). For example the composition may contain organic and/or inorganic flame retardants, fillers, processing aids and antioxidants. The amount of such additives may be for example up to 60% by weight of the composition, eg. 10 to 40%. Care should be taken to avoid the use of excessive amounts of antioxidants and other additives which inhibit cross-linking and make it necessary to use larger amounts of cross-linking agent and/or higher radiation dosages. It is an additional surprising feature of this invention that even compositions containing relatively large amounts of antioxidant, eg. 1 to 3% of the composition, can be successfully cross-linked.

Compounds which are useful as flame retardants in this invention include both halogen-containing and halogen-free retardant systems. In one embodiment the composition contains 15 to 35%, e.g. about 25%, of a halogenated, preferably brominated, organic flame retardant and 5 to 15%, e.g. about 10%, of an inorganic synergist therefor, preferably antimony trioxide, and optionally other flame retardants. In another embodiment the composition is substantially free of halogen and contains an effective amount of non-halogenated flame retardants, e.g. one or more of

- (a) a particulate salt in which the anion comprises oxygen and the cation is a metal of Group II A of the Periodic Table, e.g. basic magnesium carbonate, talc or clay;
- (b) a particulate salt in which the anion comprises boron and oxygen and the cation is a metal of Group II B of the Periodic Table, e.g. zinc borate;
- (c) a particulate compound of an element of Group IV or V of the Periodic Table, e.g. antimony trioxide; and
- (d) a particulate sulfide of a transition metal, e.g. zinc sulfide.

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We have found that excellent results can be obtained using radiation dosages of at most 12 Mrad, and often less, e.g. at most 8 Mrad or at most 6 Mrad. In order to obtain a particular degree of cross-linking, the radiation dose required is dependent on the amount and type of cross-linking agent present. The cross-linking agent and radiation dose are selected so that the cross-linked article has an  $M_{100}$  value above its melting point, of at least  $2.1 \text{ kg/cm}^2$ , generally 2.1 to 10.5  $\text{kg/cm}^2$ , preferably 2.6 to 4.2  $\text{kg/cm}^2$ , and/or an  $E_{30}$  value above its melting point, of at least  $5.6 \text{ kg/cm}^2$ , preferably 5.6 to 17.5  $\text{kg/cm}^2$ . The  $M_{100}$  and  $E_{30}$  values referred to herein are measured by a modulus test carried out at an elevated temperature above the melting point of the article, i.e. after melting is completed and, if the article is heat-recoverable, after it has been heat-recovered in the absence of any restraint. In this test, the stress required to elongate a specimen of the cross-linked article by 30 and 100% is measured, using an Instron tester at a crosshead speed of 5.1 cm (2 inch)/minute, a jaw separation of 4.8 cm (1.9 inch) and a chart speed of 12.7 cm (5 inch)/minute. A specimen, usually a strip 0.6 or 1.27 cm (0.25 or 0.5 inch) wide, cut from the cross-linked article is clamped at the top and allowed to equilibrate at the elevated temperature, and the lower end is then clamped. The force required to elongate the specimen to 30% and to 100% is recorded. The  $E_{30}$  and  $M_{100}$  values are then calculated as follows

$$E_{30} = \frac{\text{Force at 30% elongation}}{\text{Initial cross-sectional area of specimen}} \times \frac{1.30}{0.30}$$

$$M_{100} = \frac{\text{Force at 100% elongation}}{\text{Initial cross-sectional area of specimen}}$$

Articles prepared by cross-linking according to the invention can readily be converted into heat-recoverable articles by methods well known in the art. Preferred recoverable articles of the invention are hollow and heat-shrinkable, eg. tubing. Such an article may contain or have a coating on at least a part of its inner surface of a material which flows at the recovery temperature of the article, eg. Nylon-12 which is substantially free from cross-linking or has been cross-linked only to a limited extent which does not prevent it from flowing at the recovery temperature.

The invention is illustrated by the following Examples, which are summarised in Table 1, 2, 3 and 4 below, Examples 1, 2 and 16 being comparative Examples outside the scope of the invention.

In each of the Examples, the indicated amounts (in parts by weight) of the indicated ingredients were mixed together in a ZSK extruder, extruded into a water bath and cut into pellets. After drying, the pellets were melt-shaped, in Examples 1 to 23 into slabs 15.2 x 15.2. x 0.0635 cm (6.0 x 6.0 x 0.025 inch), using a heated press at 2100 kg/cm<sup>2</sup> (30,000 psi) pressure and a temperature 200° C, and in Examples 24 to 36 into tubing having an internal diameter of 0.32 cm (0.125 inch) and a wall thickness of 0.056 cm (0.022 inch), using a single screw extruder. The shaped articles were then irradiated to the indicated dose, using a beam of high energy electrons. The indicated properties of the cross-linked product were

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then measured. The cross-linked tubing produced in Examples 24 to 26 was converted into heat-shrinkable tubing by expanding it to an internal diameter of 0.635 cm (0.25 inch) in a glycerine bath.

The Nylon-11 used in Examples 1 to 15 and 20-26 was the product sold by Rilsan Corporation under the trade name BESNO, which is believed to be substantially pure polyundecanoamide. The plasticised Nylon-11 used in Examples 27 and 28 was the product sold by Rilsan Corporation under the trade name BESNO-P40 which is a plasticised polyundecanoamide. The stabilized Nylon-11 used in Examples 29 to 36 was the product sold by Rilsan Corporation under the trade name BESNO-TL, which is a light- and heat-stabilized polyundecanoamide. The Nylon-12 used in Examples 16 to 19 was the product sold by Huls under the trade name L-2101, which is believed to be substantially pure polydodecanoamide. The antioxidant used in Examples 37 to 39, Cyanox 1212, is available from American Cyanamid and is believed to be a mixture of distearyl thio-di-propionate and dilauryl thio-di-propionate. The antioxidant used in Example 37, Goodrite 3114, is available from B. F. Goodrich and is tris (3,5-di-t-butyl-4-hydroxybenzyl) isocyanurate. The antioxidant used in Example 38, Goodrite 3125, is available from B. F. Goodrich and is 3,5-di-t-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris (2 hydroxyethyl)-S-triazine-2,4,6 ( $1\text{H},3\text{H},5\text{H}$ -trione). The antioxidant used in Example 39, Irganox 1010, is available from Ciba-Geigy and is tetrakis[methylene 3-(3<sup>1</sup>,5<sup>1</sup>-di-t-butyl-4<sup>1</sup>-hydroxyphenyl) propionate]methane.

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TABLE 1

<u>Example No.</u>	<u>1(c)</u>	<u>2(c)</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>
Nylon-11	99	100	99	99	99	99	99	98	98	98	98	96	99	98	96
Triallyl isocyanurate	1	-	1	1	1	1	1	2	2	2	2	4	-	-	-
Triallyl cyanurate	-	-	-	-	-	-	-	-	-	-	-	1	2	4	
Radiation Dose (Mrad)	0	10	0.5	1	2	4	10	0.5	1	2	10	10	10	10	10
$M_{100}$ at 200°C (kg/cm <sup>2</sup> )	melted	melted	5.0	9.1	10.7	10.4	11.0	5.5	8.2	9.6	10.9	25.3	3.2	9.8	9.8

TABLE 2

<u>Example No.</u>	<u>16(c)</u>	<u>17</u>	<u>18</u>	<u>19</u>
Nylon-12	100	99	98	96
Triallyl isocyanurate	0	1	2	4
Radiation Dose (Mrad)	10	10	10	10
$M_{100}$ at 200°C (kg/cm <sup>2</sup> )	melted	9.1	14.9	28.4

TABLE 3

<u>Example No.</u>	<u>20</u>	<u>21</u>	<u>22</u>	<u>23</u>
Nylon-11	80	82	82	82
Antimony trioxide	5	5	5	5
Magnesium Carbonate	7	-	-	-
Zinc Borate	5	-	-	-
Bromine-containing organic flame retardant:	-	10	10	10
Triallyl isocyanurate	3	3	3	3
Radiation Dose (Mrad)	10	10	10	10
$M_{100}$ at 200° C (kg/cm <sup>2</sup> )	13.5	11.7	11.7	11.4
Oxygen Index	23	24.5	22	25

TABLE 4

<u>Example No.</u>	<u>24</u>	<u>25</u>	<u>26</u>	<u>27</u>	<u>28</u>	<u>29</u>	<u>30</u>	<u>31</u>	<u>32</u>	<u>33</u>	<u>34</u>	<u>35</u>	<u>36</u>
Nylon-11	97	97	97	-	-	-	-	-	-	-	-	-	-
Plasticised Nylon-11	-	-	-	98	98	-	-	-	-	-	-	-	-
Stabilised Nylon-11	-	-	-	-	-	97	97	97	97	98	98	98	99
Triallyl isocyanurate	3+	3+	3+	2	2	3+	3+	3+	3+	2	2	2	1
Radiation Dose	6	1.8	0.64	3.5	10.8	8	3.2	2.0	1.8	2.3	1.6	3.5	6.7
$E_{30}$ at 200° C (kg/cm <sup>2</sup> )	31.9	26.0	15.8	5.5	5.3	20.8	14.4	10.1	9.9	11.9	9.1	14.4	7.6
$M_{100}$ at 200° C (kg/cm <sup>2</sup> )	-	13.2	8.5	3.4	2.4	10.2	7.6	5.3	5.3	-	-	-	3.2

TABLE 5

<u>Example No.</u>	<u>37</u>	<u>38</u>	<u>39</u>	
Stabilized Nylon-11		95.5	95.5	95.5
Triallyl isocyanurate	3	3	3	
Antioxidant				
Cyanox 1212		0.5	0.5	0.5
Goodrite 3114	1	-	-	
Goodrite 3125	-	1	-	
Irganox 1010	-	-	1	
Radiation Dose (Mrad)	18	18	18	
$M_{100}$ at 200° C (kg/cm <sup>2</sup> )	7.1	19.5	8.5	

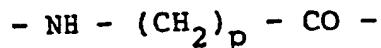
CLAIMS

1. An article, especially a heat-recoverable article, composed of a radiation cross-linked polymeric composition which

(a) has been cross-linked by radiation in the presence of an unsaturated radiation cross-linking agent,

(b) has an  $M_{100}$  value above its melting point of at least 2.1 kg/cm<sup>2</sup>, preferably 2.1 to 10.5 kg/cm<sup>2</sup>, particularly 2.6 to 4.2 kg/cm<sup>2</sup>, and

(c) comprises a cross-linked organic polymer component which comprises at least 80%, preferably substantially 100%, by weight of at least one polyamide consisting essentially of monomer units which are linked to each other through amide linkages, at least 25%, preferably at least 75%, by weight of the monomer units having the formula



where p is 11 or 12.

2. An article according to Claim 1 wherein the polymer component consists essentially of 75 to 100% by weight of Nylon-11 or Nylon-12 or a mixture thereof and 0 to 25% by weight of Nylon-6, Nylon-6,6, Nylon 6,9, Nylon 6,10, or Nylon 6,12 or a blend of two or more of these.

3. An article according to Claim 1 or 2 which is hollow and heat-shrinkable and which has a coating on its inner surface of a material which flows at the recovery temperature of the article.

4. A process for the manufacture of a cross-linked article as claimed in any one of claims 1 to 3, which process comprises the steps of

(1) melt-shaping a polymeric composition comprising

(a) an organic polymer component which comprises at least 80%, preferably at least 90% by weight of at least one polyamide consisting essentially of monomer units which are linked to each other through amide linkages, at least 25%, preferably at least 75%, by weight of the monomer units having the formula  
$$- \text{NH} - (\text{CH}_2)_p - \text{CO} -$$
where p is 11 or 12; and

(b) an unsaturated radiation cross-linking agent for said polymer; and

(2) irradiating the shaped article prepared in step (1) to effect cross-linking thereof.

5. A process according to Claim 4 wherein the irradiation is carried out in air.

6. A process according to Claim 4 or 5 wherein the cross-linking agent consists of elements selected from carbon, hydrogen, oxygen and nitrogen, especially triallyl isocyanurate or triallyl cyanurate or a mixture thereof.

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7. A process according to Claim 4, 5 or 6 wherein the amount of said cross-linking agent is less than 4%, preferably less than 2%, by weight, based on the weight of the organic polymer component.

8. A process according to Claim 7 wherein the shaped article is irradiated to a dose of at most 12 Mrad, preferably at most 8 Mrad.

9. A process according to any one of claims 4 to 8 which further comprises the steps of

- (3) heating the cross-linked article above its melting point;
- (4) deforming the article while it is at a temperature above its melting point; and
- (5) cooling the article while it is in the deformed condition;

whereby a heat-recoverable article is prepared.

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⑯ Priority: 03.12.80 US 212483

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⑯ Designated Contracting States: **AT BE CH DE FR IT LI NL SE**

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⑯ Article comprising conductive polymers and process for making the same.

⑯ Polyamides comprising substantial amounts of Nylon-11 and/or Nylon-12 units are cross-linked by irradiation in the presence of an unsaturated cross-linking agent, preferably triaryl isocyanurate. The cross-linked products are particularly useful in the form of heat-recoverable shaped articles, e.g. heat-shrinkable tubing.

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. *)
X, Y	GB-A-1 184 599 (RAYCHEM) * Page 1, line 79 - page 3, line 16; examples; claims *	1-9	B 29 C 25/00 C 08 G 69/48
Y	--- DE-A-1 569 349 (RAYCHEM) * Claims; page 2, paragraph 2 - page 5, paragraph 1; examples *	4-9	
Y	--- GB-A-1 116 879 (RAYCHEM) * Claims; page 3, line 58 - page 4, line 41; examples *	3	
A	--- DE-A-2 041 989 (MITSUI MINING) * Claims; page 6, paragraph 4 - page 7, paragraph 1 *	2	
	-----		TECHNICAL FIELDS SEARCHED (Int. Cl. *)
			B 29 C 25/00 C 08 G 69/00
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	04-04-1984	VANHECKE H.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
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